GTT Annual Workshop and User Meeting
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Modelling Internal Corrosion of High Temperature Alloys

Ulrich Krupp

Hochschule Osnabrück
University of Applied Sciences

Institute of
Materials Design and
Structural Integrity

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Katrin Jahns
Institute of Materials Design and Structural Integrity

Martin Landwehr, Prof. Dr. Jürgen Wübbelmann
Institute of Computer Engineering

University of Applied Sciences Osnabrück, Germany

Dr. S.-Y. Chang, Dr. Robert Orosz, Dr. Vicente Trindade,
Prof. H.-J. Christ

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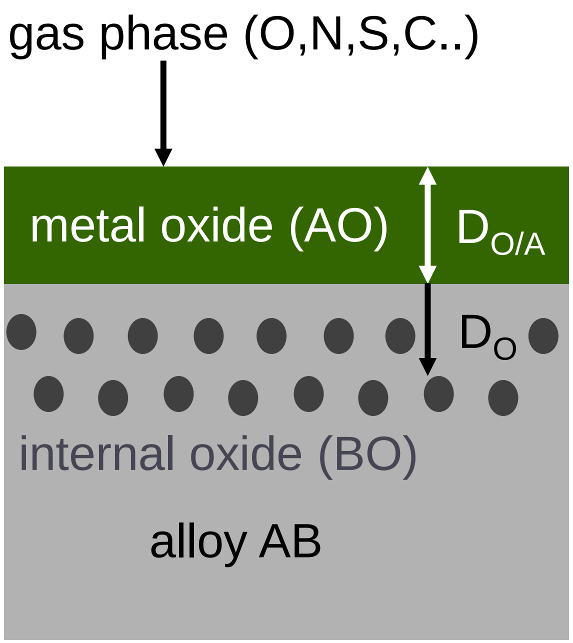
Outline

- What is Internal Corrosion?
- Wagner's Theory of Internal Oxidation
- Limitations of the Classical Theory
- Numerical Treatment of Internal Oxidation and Nitridation
  - Finite Difference
  - Cellular Automata

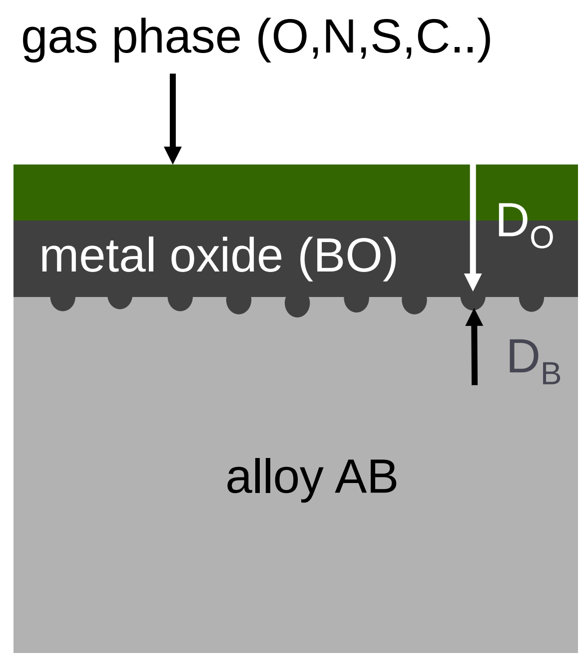
What is Internal Corrosion?

high-temperature corrosion:

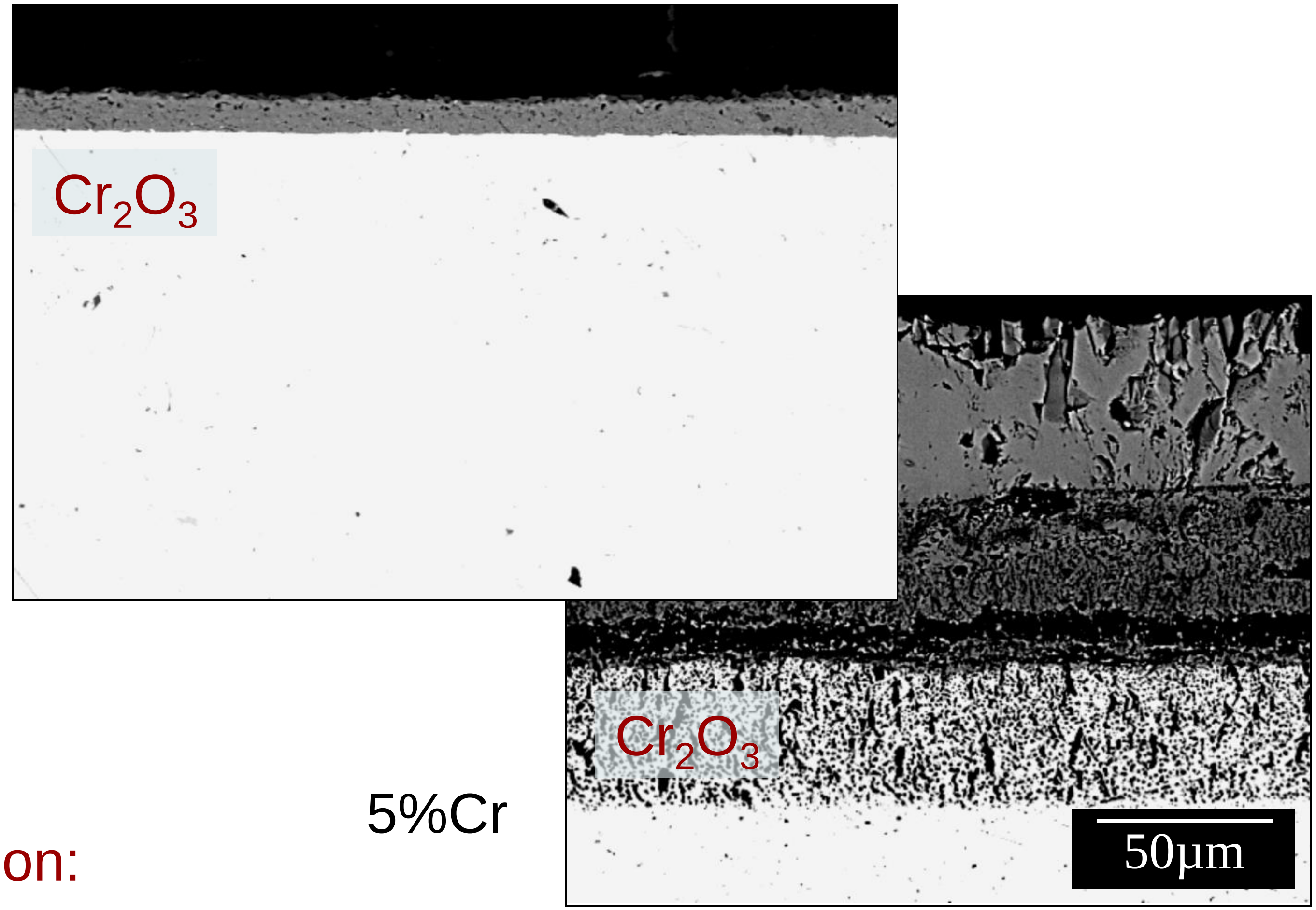
superficial scale + internal oxidation



selective oxidation



Transition from Internal to External Oxidation
Oxidation of Ni-Cr Alloys (100h, 1000°C, air)



20%Cr

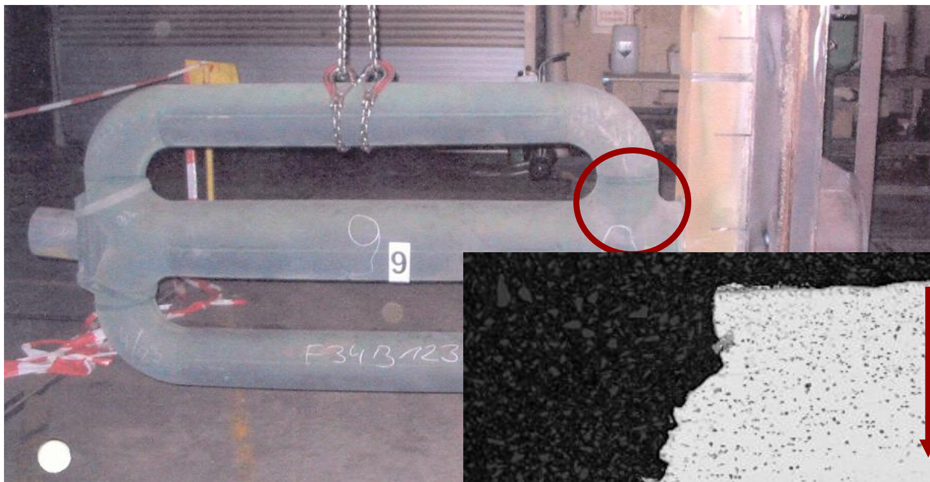
5%Cr

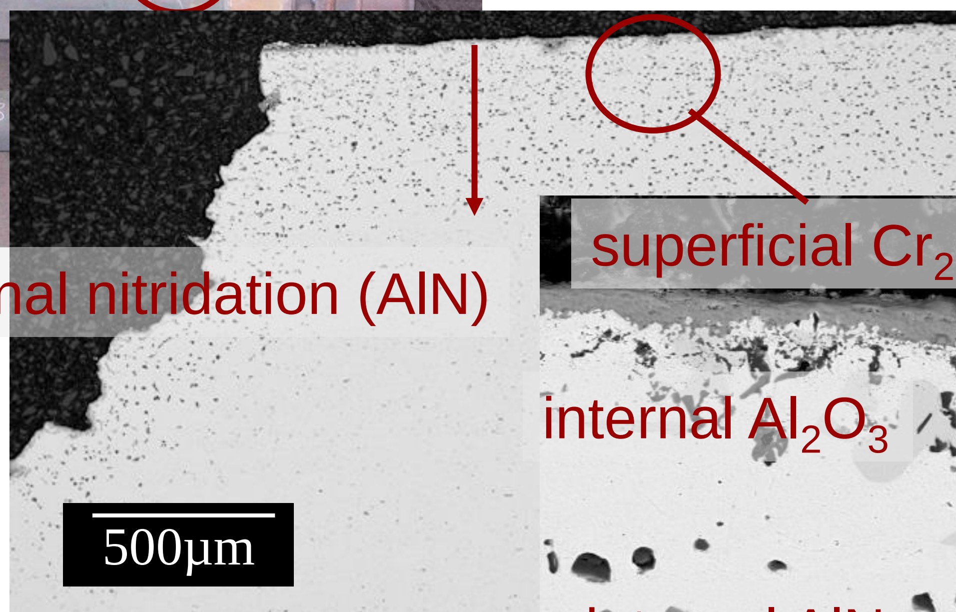
depends on:
$c_{Cr}/D_{Cr}/T$

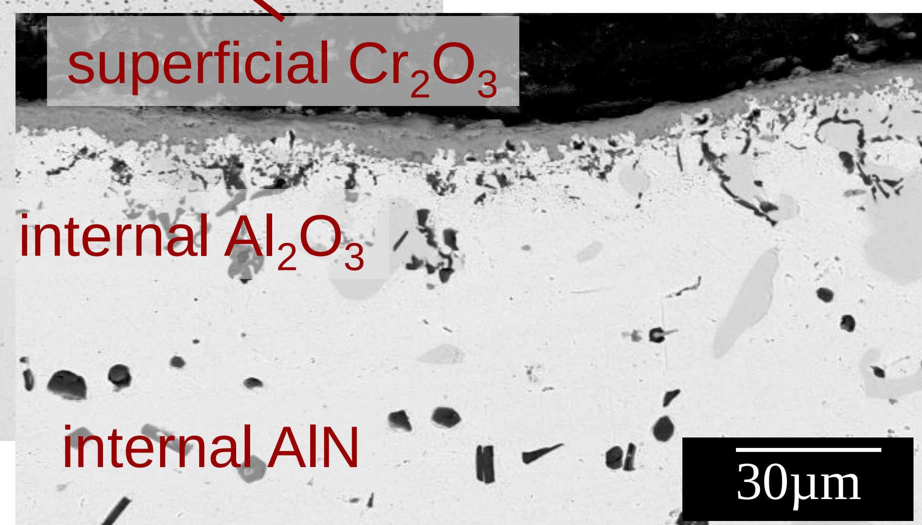
Material Degradation by Internal Corrosion

gas and steam turbines, heat exchangers, chemical reactors, exhaust systems, metallurgy, heat treatment …

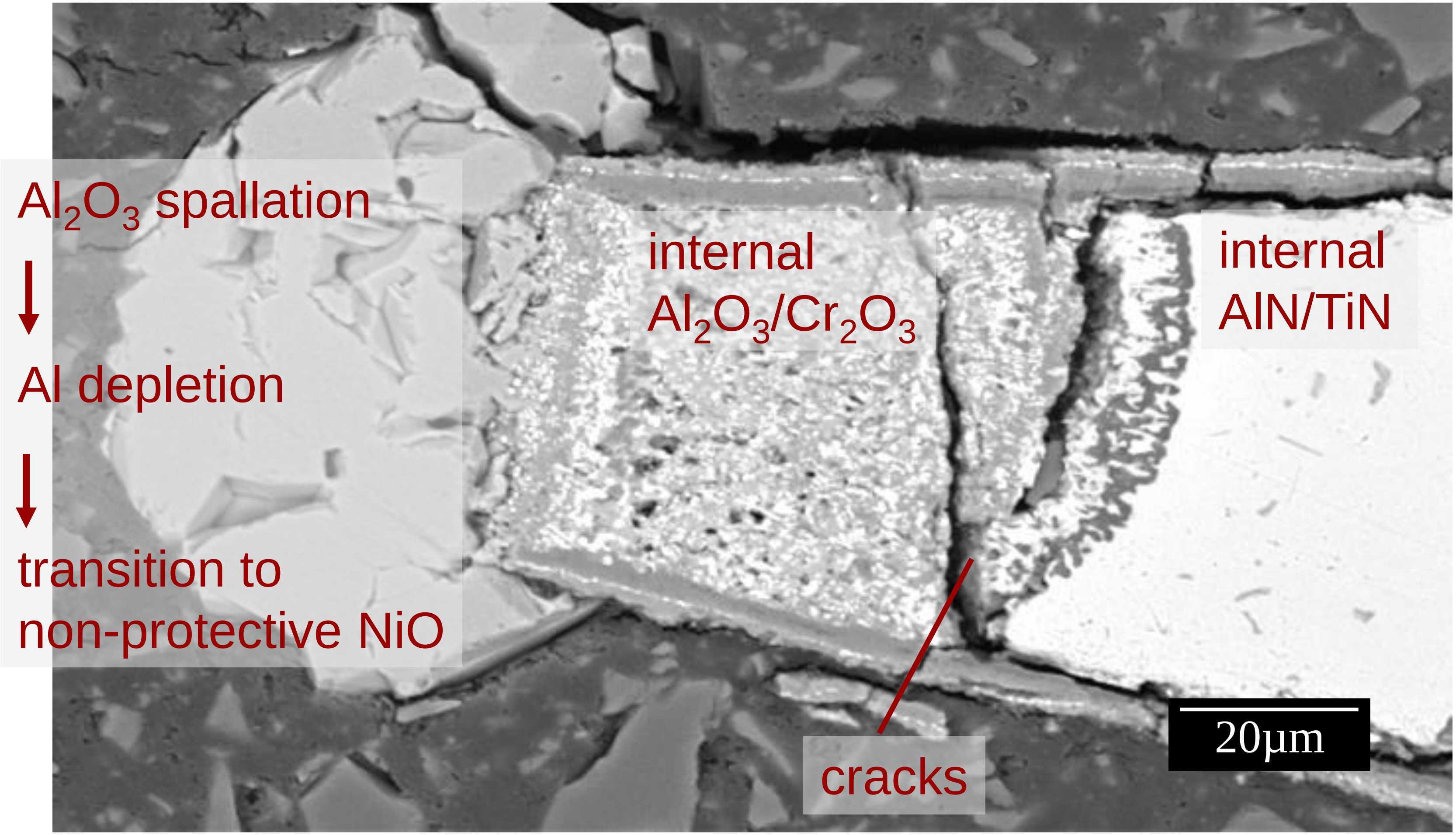
(Natural Gas Burner Tube, alloy 601)

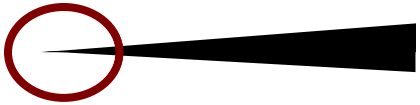






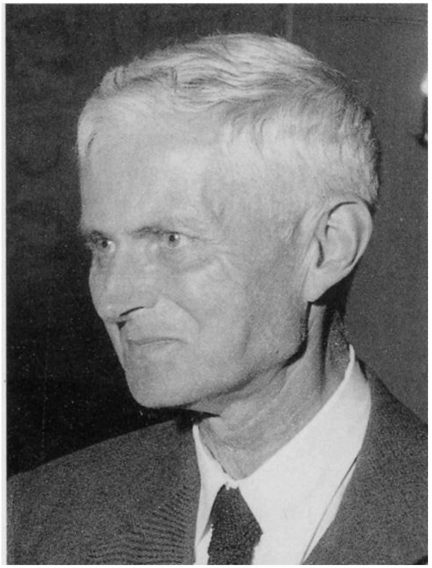
Material Degradation during Cyclic Oxidation at 1100°C



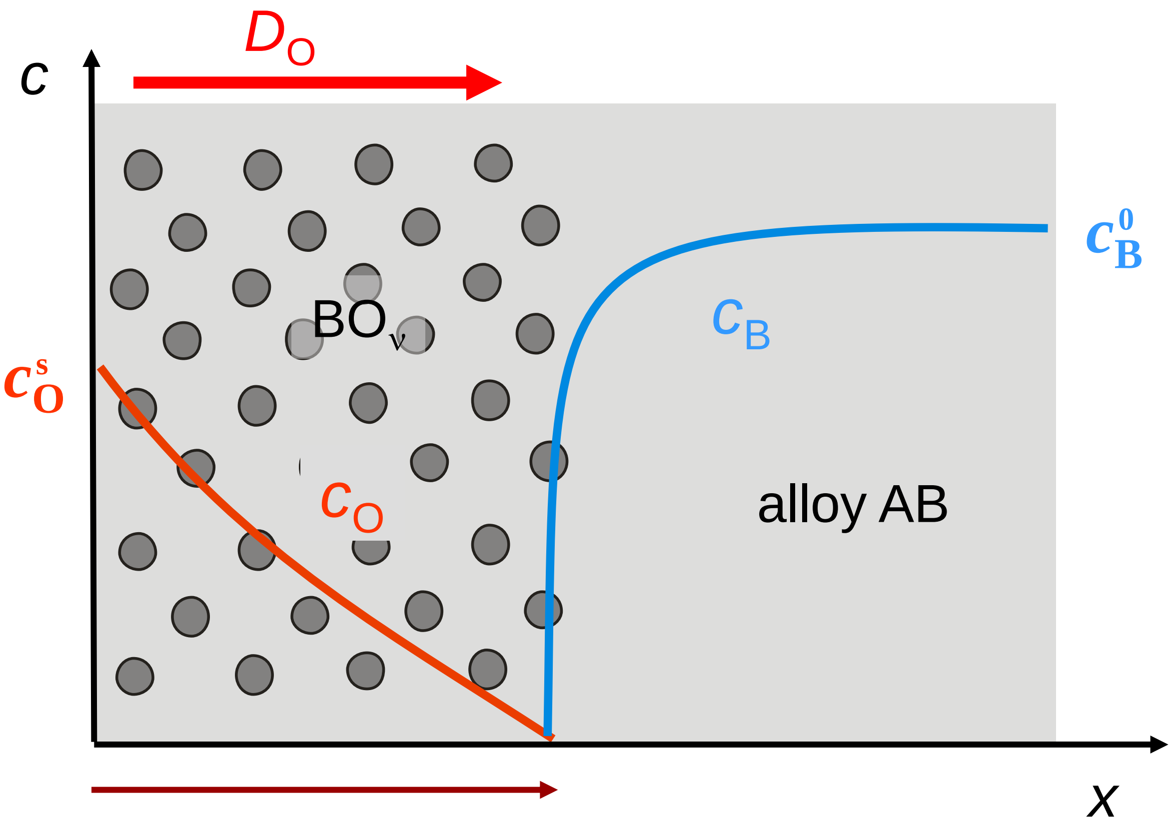


Wedge-Shaped Specimen CMSX-4 at 1100°C

Carl Wagner's Theory of Internal Oxidation



Carl W. Wagner (1901-1977)



Depth of the Internal Precipitation Zone ξ

$$\xi^2 = \frac{2c_O^s D_O}{\nu c_B^0} t \quad \text{for} \quad D_B / D_O << c_O^s / c_B^0 << 1$$

C. Wagner, Z. Elektrochemie, 21 (1959) 773

Carl Wagner's Theory of Internal Oxidation

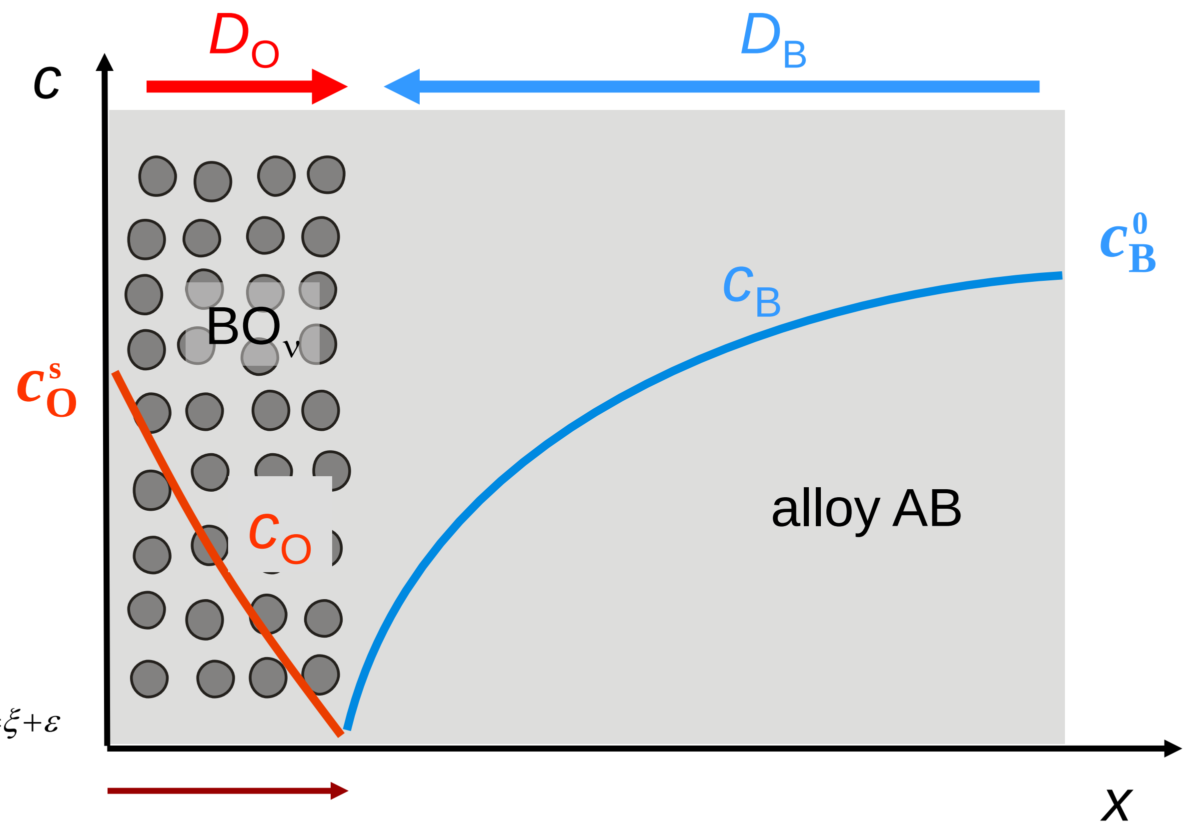
Diffusion of O and B:

$$c_O = c_0^s\left(1 - \frac{\operatorname{erf}\left(x/2\sqrt{D_O t}\right)}{\operatorname{erf}\,\gamma}\right)$$

$$c_B = c_B^0\left(1 - \frac{\operatorname{erfc}(x/2\sqrt{D_B t})}{\operatorname{erfc}\,(\gamma\sqrt{D_O/D_B})}\right)$$

Mass Balance at ξ:

$$-D_O\left(\frac{\partial c_O}{\partial x}\right)_{x=\xi-\varepsilon} = \nu D_B\left(\frac{\partial c_B}{\partial x}\right)_{x=\xi+\varepsilon}$$



Depth of the Internal Precipitation Zone ξ

$$\xi^2 = \pi\frac{D_O^2}{D_B}\left(\frac{c_O^s}{\nu c_B^0}\right)^2 t \quad \text{for} \quad \gamma << 1 \quad \gamma\sqrt{D_O/D_B} << 1$$

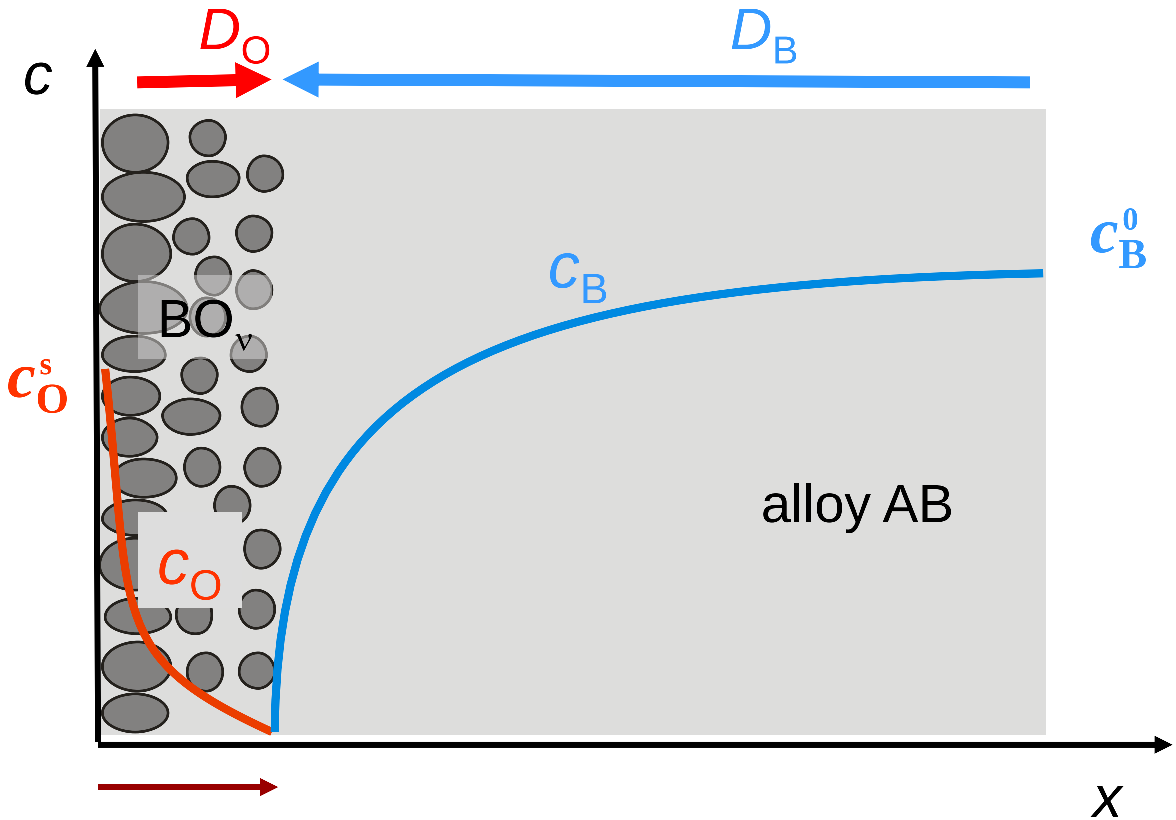
C. Wagner, Z. Elektrochemie, 21 (1959) 773

Carl Wagner's Theory of Internal Oxidation

Mass Balance:

Mole fraction BO_ν ⇔
B flux to reaction front

$$\frac{fAd\xi}{V_m} = \left[\frac{AD_B}{V_m} \frac{\partial c_B}{\partial x} \right] dt$$



Transition from Internal to External Oxidation

$$c_B^0 > \pi \left[\frac{\pi g^*}{2\nu} c_O^s \frac{D_O V_m}{D_B V_{Ox}} \right]$$ with g^*: crit. volume fraction of oxide

C. Wagner, Z. Elektrochemie, 21 (1959) 773

Limitations of Wagner's Analytical Approach

One type of precipitates of high thermodynamic stability (solubility product $K_{SP} = N_{\mathrm{B}} N_{\mathrm{O}}^{\nu} \approx 0$)

Constant boundary conditions - no changes in temperature, gas composition etc. possible

Effective diffusivity - through complex microstructure, e.g., $D_{\mathrm{GB}} > D_{\mathrm{bulk}}$

One-dimensional - nucleation and growth kinetics / changes in the diffusion path are neglected

Nucleation and Growth of Internal Precipitates

(TiN and AlN in NiCr20Al2Ti2, 1000°C, 150h, N_2)

Energy Balance:

interface energy γ

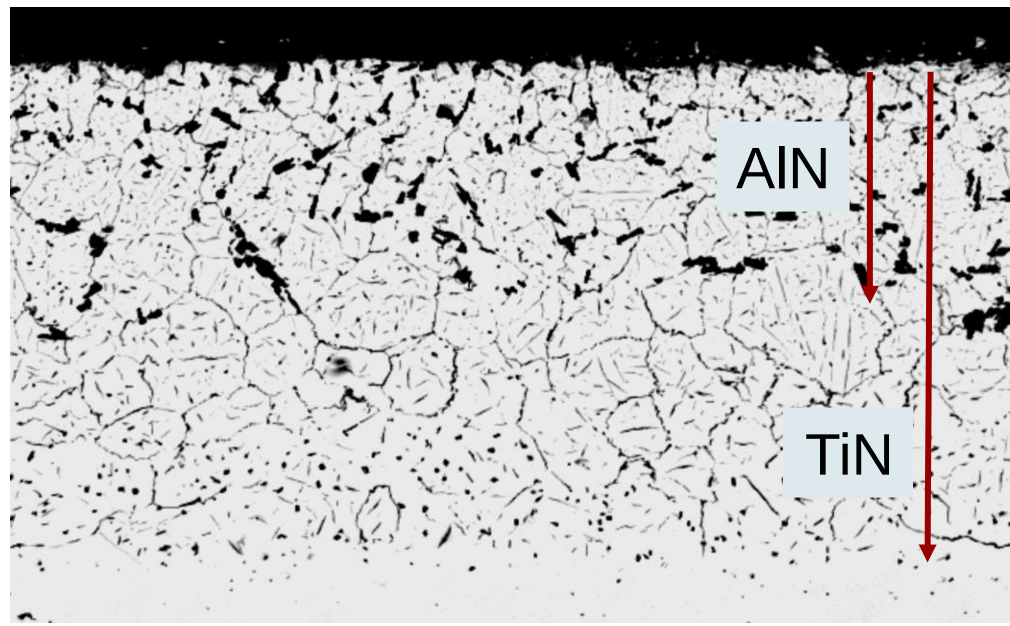
free energy change ΔG

strain energy ΔG_s

(defect site annilhilation energy)

$$\Delta G = \boxed{V\left(\Delta G_V\right.} + \Delta G_s \left.\right) + \boxed{\sum_i A_i \gamma_i}$$

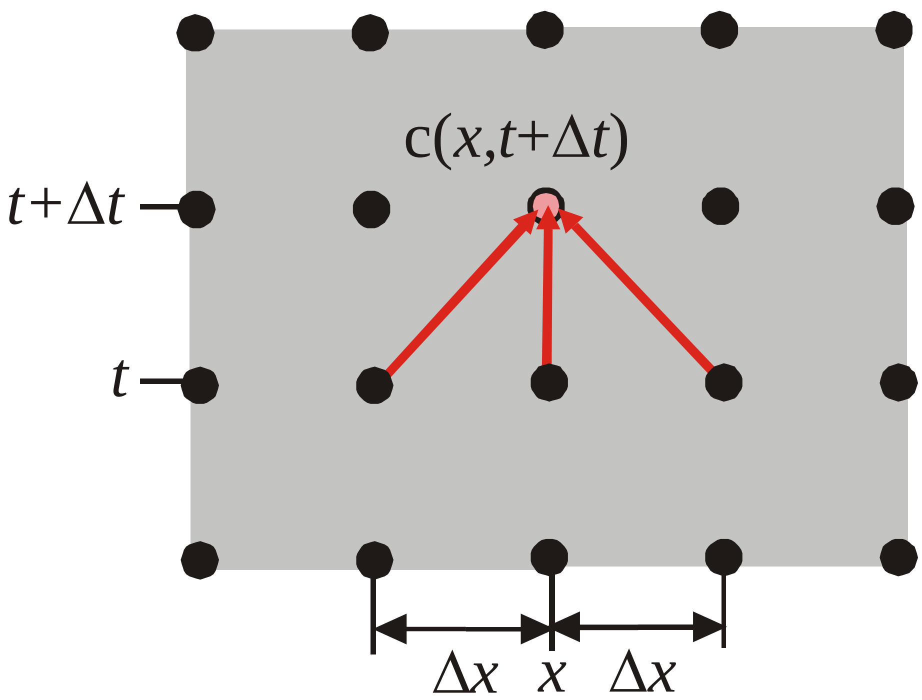
Supersaturation



G. Böhm, M. Kahlweit, Acta Met., 12 (1964) 641

D. J. Young: High Temperature Oxidation and Corrosion of Metals, Elsevier 2008

Finite-Difference Treatment of Diffusion



$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

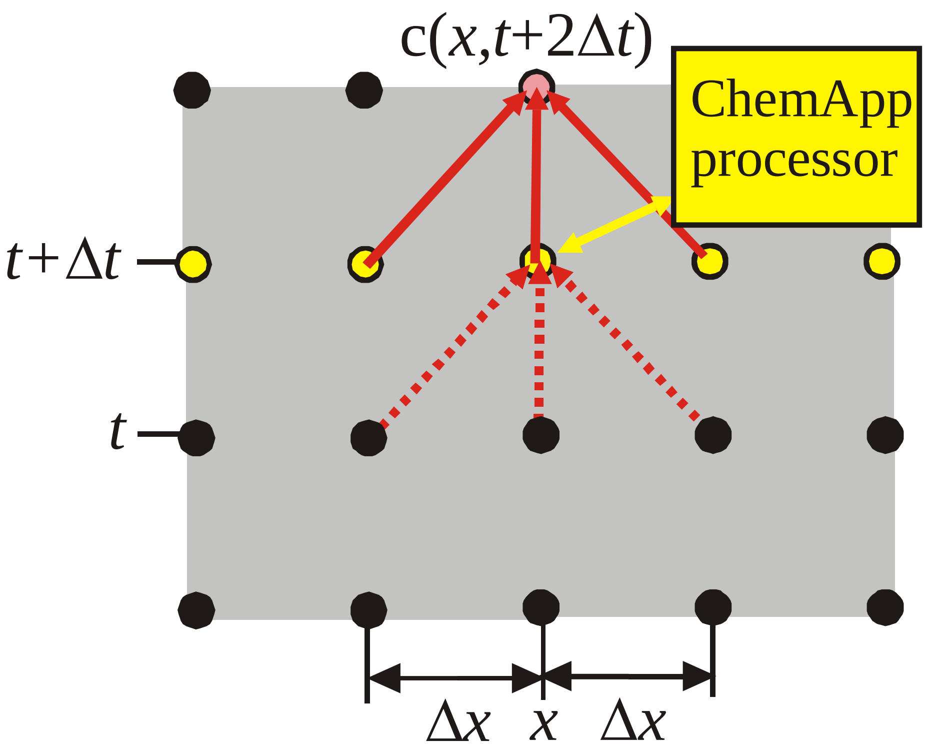
$$\left(\frac{\partial c}{\partial t}\right)_{x,t} \approx \frac{c(x,t+\Delta t)-c(x,t)}{\Delta t}$$

$$\left(\frac{\partial^2 c}{\partial t^2}\right)_{x,t} \approx$$

$$\approx D\frac{c(x+\Delta x,t)-2c(x,t)+c(x-\Delta x,t)}{\Delta x^2}$$

$$c_i(x,t+\Delta t) = c(x,t) + \frac{D\Delta t}{\Delta x^2}\left[c(x-\Delta x,t)-2c(x,t)+c(x+\Delta x,t)\right]$$

Finite-Difference Treatment of Diffusion



computational thermodynamics
ChemApp + system data
(GTT technologies)

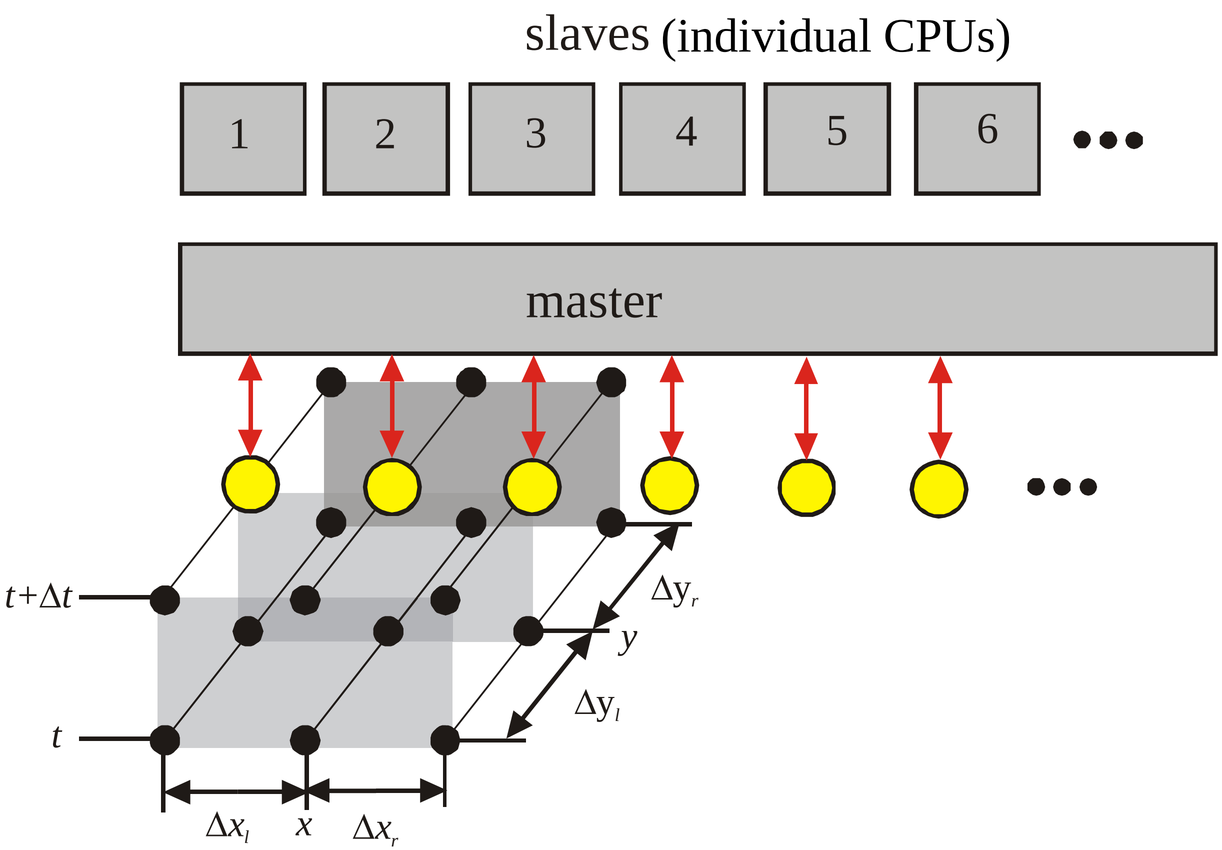
$$G = \sum_{j=1}^{m} c_j \left(G_{j,\mathrm{pure}} + G_{j,\mathrm{id}} + G_{j,\mathrm{non\text{-}id}} \right)$$

= min !

$$c(x, t+\Delta t) = c(x,t) + \frac{D\Delta t}{\Delta x^2}\left[c(x-\Delta x, t) - 2c(x,t) + c(x+\Delta x, t) \right]$$

Krupp et al., Mater. Corr., **57** (2006) 263
U. Buschmann , Dissertation, Univ. Siegen 2008

2D Finite-Difference Treatment of Diffusion
(Crank Nicolson implicit approach)



D=f(x,y)
(e.g. PVM)

bulk and gb diffusion

Parallelization
(e.g. PVM, GPU/CUDA)

ChemApp / system data base initialisation

distributed equilibrium calculations

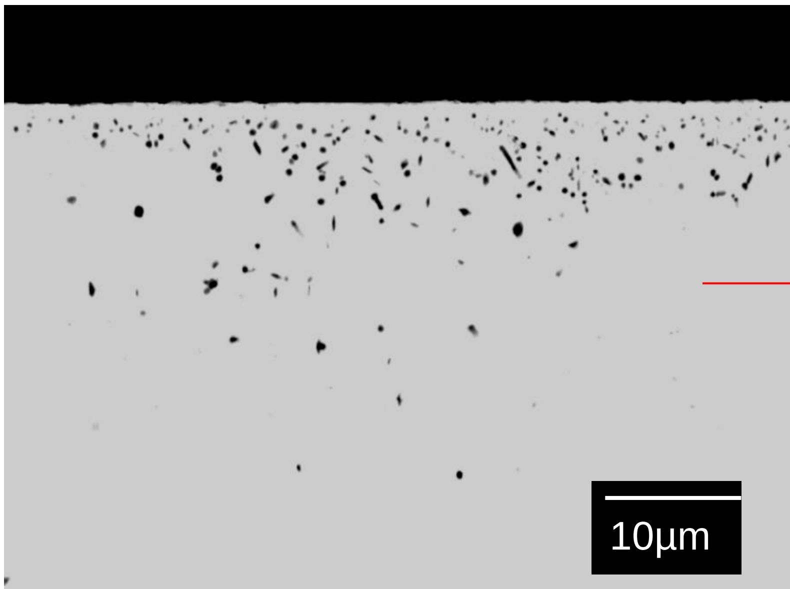
C – Main program

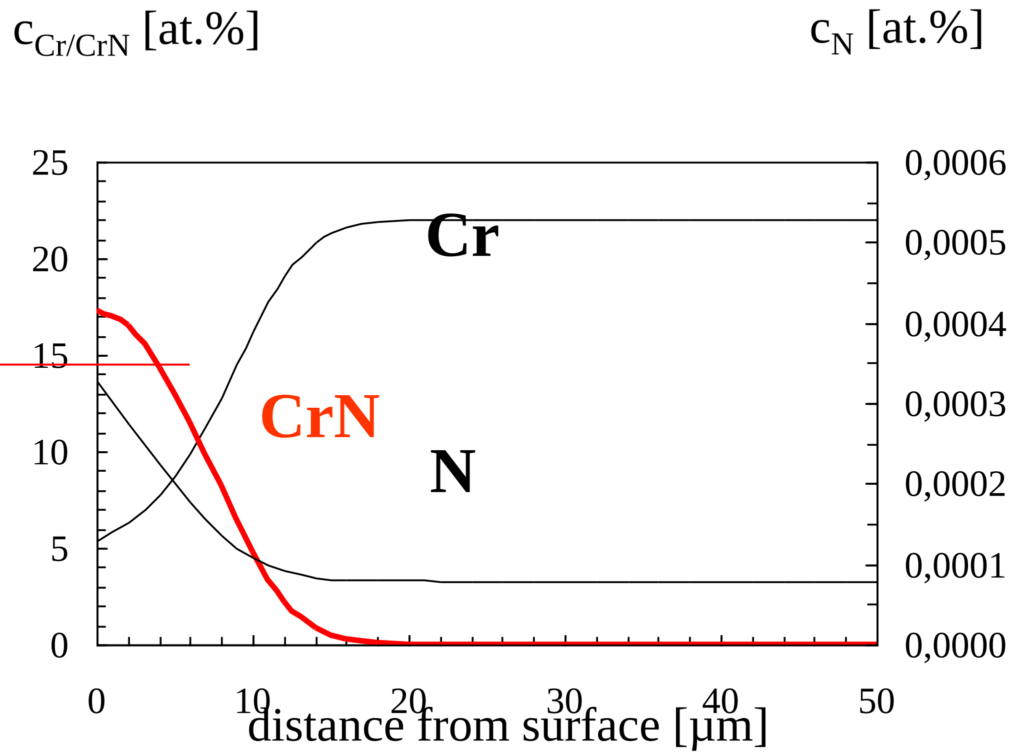
FD diffusion calculation

user interface

Krupp et al., Mater. Corr., **57** (2006) 263

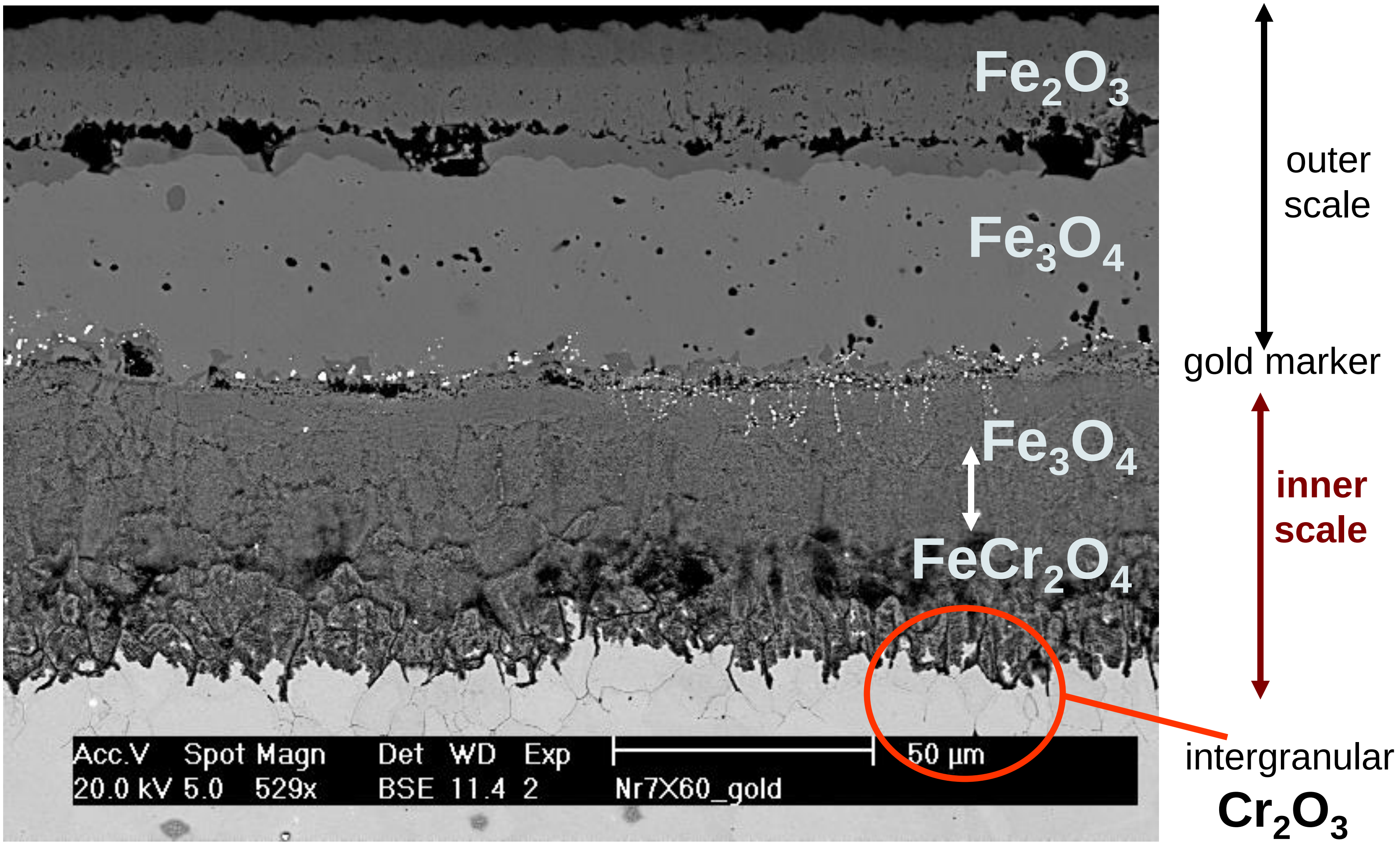
Finite-Difference Simulation of Internal Precipitation of Cr-Nitrides of Moderate Stability (NiCr20, 800°C, N_2)





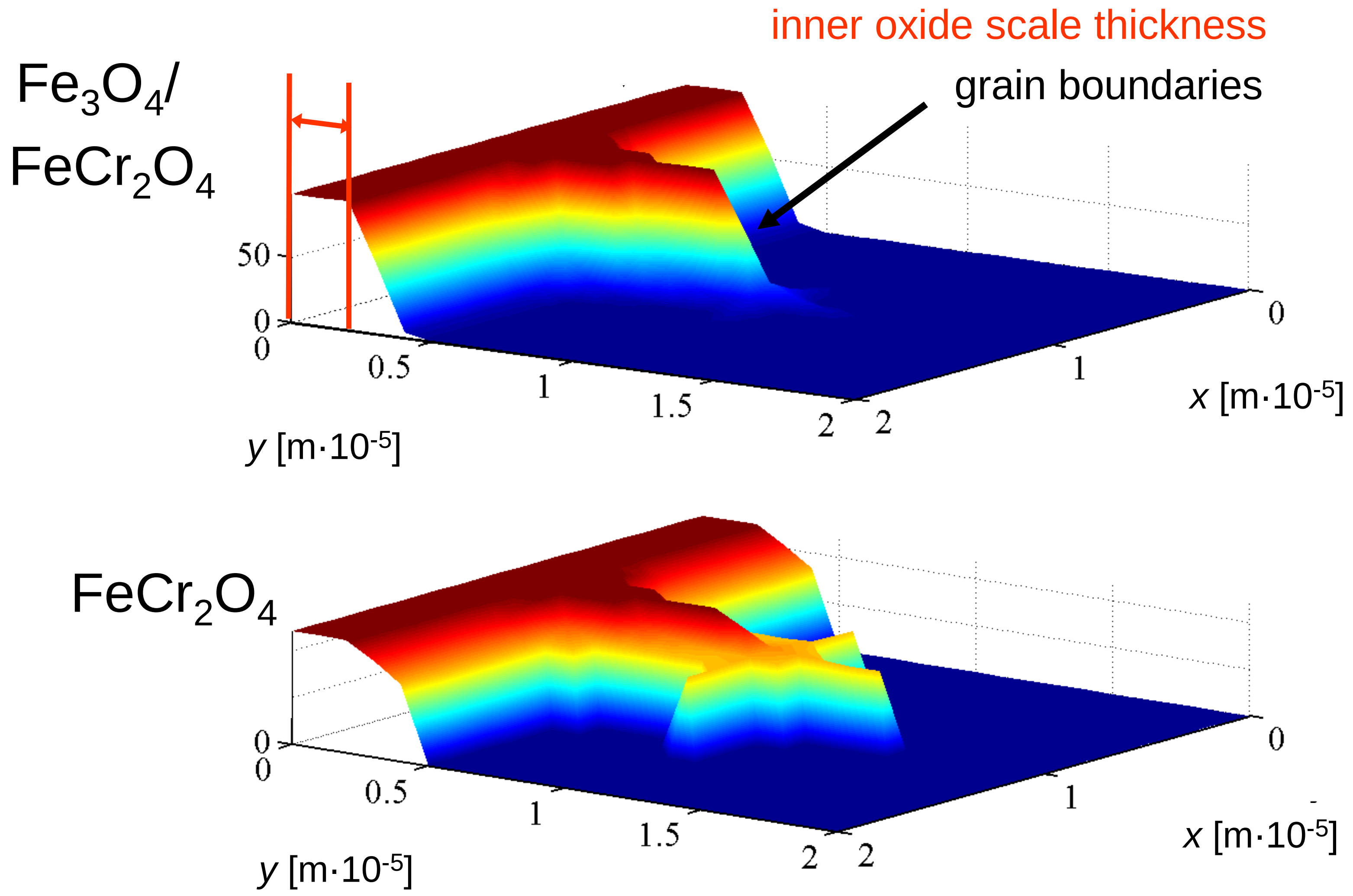
Oxidation of Low-Cr Steels (X60)

(1.43wt% Cr, 550°C, air)

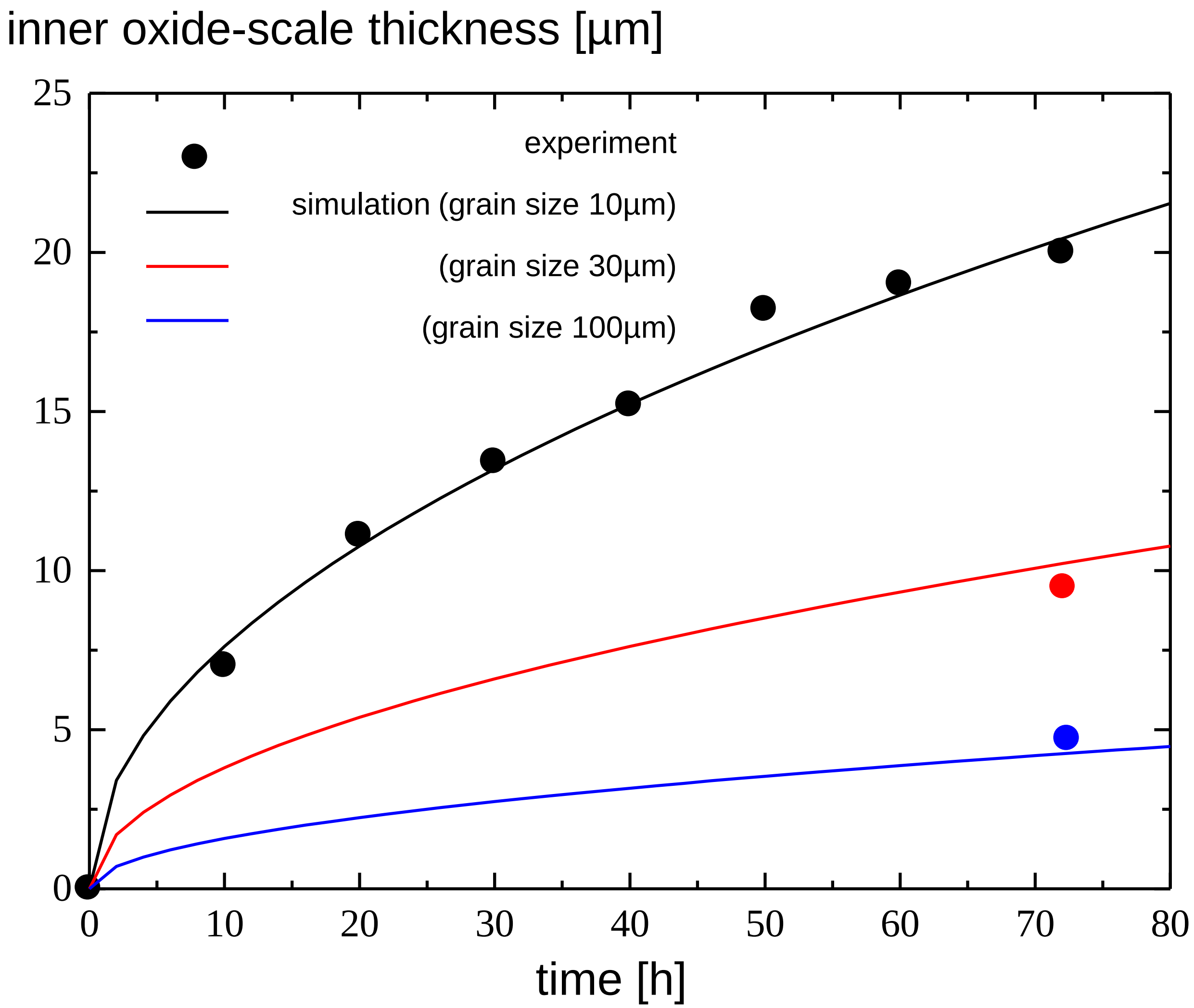


V. Trindade, PhD thesis 2006

2D Simulation of Internal Oxidation

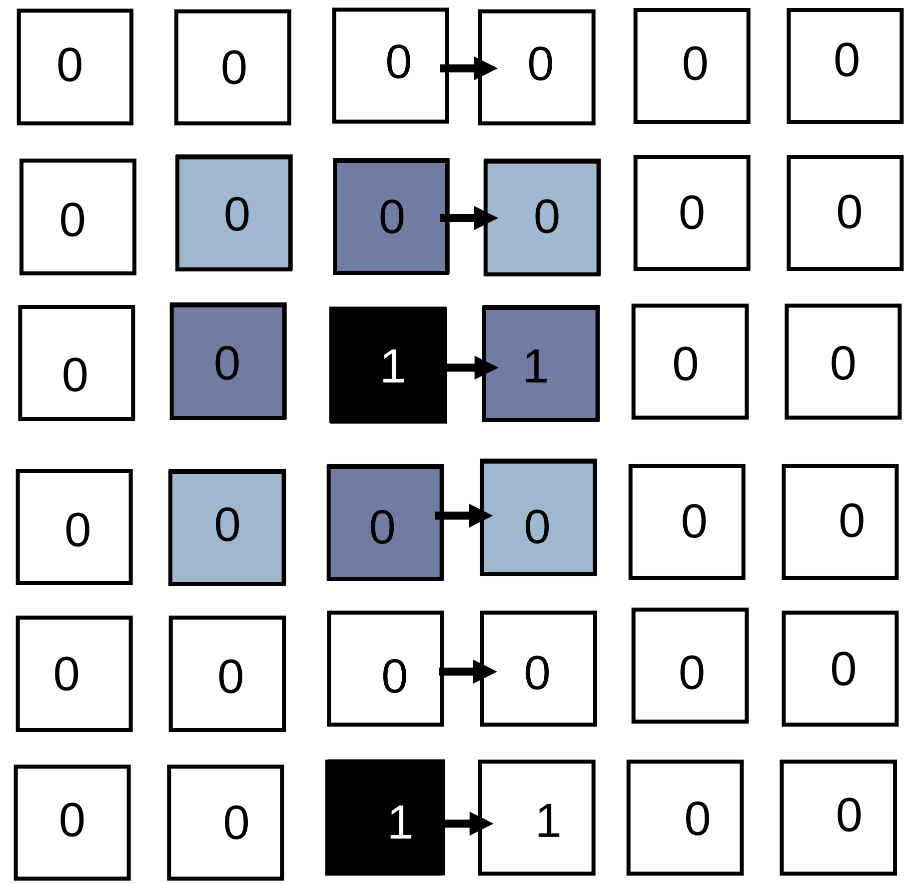


Inner Oxide-Scale Growth (X60)



(1.43wt% Cr, 550°C, air)

The Cellular Automata Approach



Dividing Space into Lattice

Defining a Neighbourhood
(von Neumann, Moore)

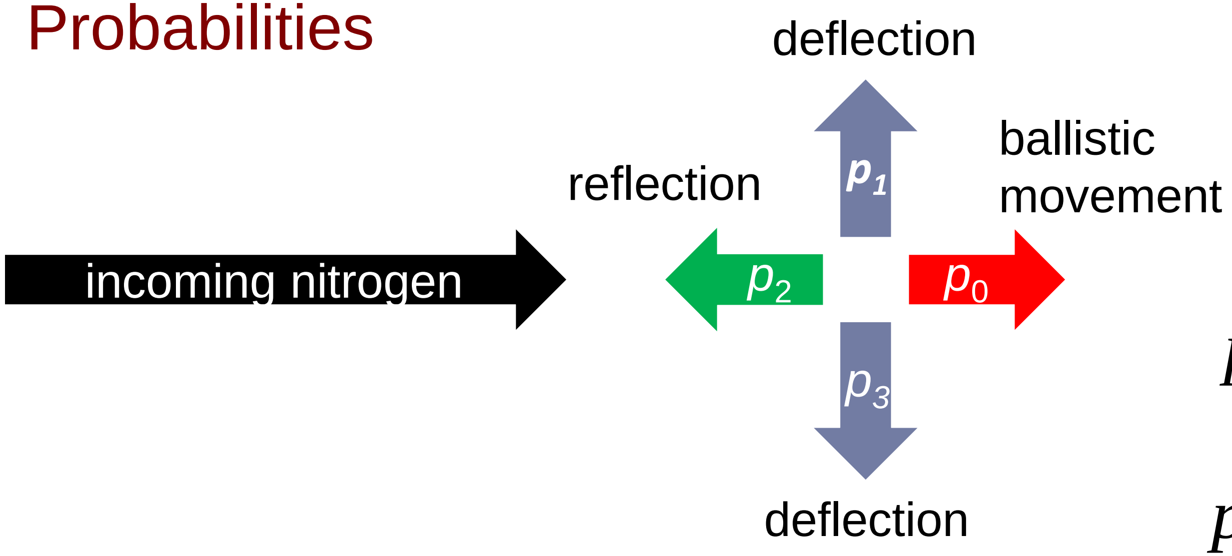
Defining State Variables
(e.g.: 0,1)

Defining Transition Rules
(applied simultaneously to all cells)

cf. Rapaz, Bellet, Deville: Numerical Modeling in MSE, Springer 1998

The Cellular Automata Approach (Chopard and Droz)

Probabilities



$$p_1 = p_3 = p$$

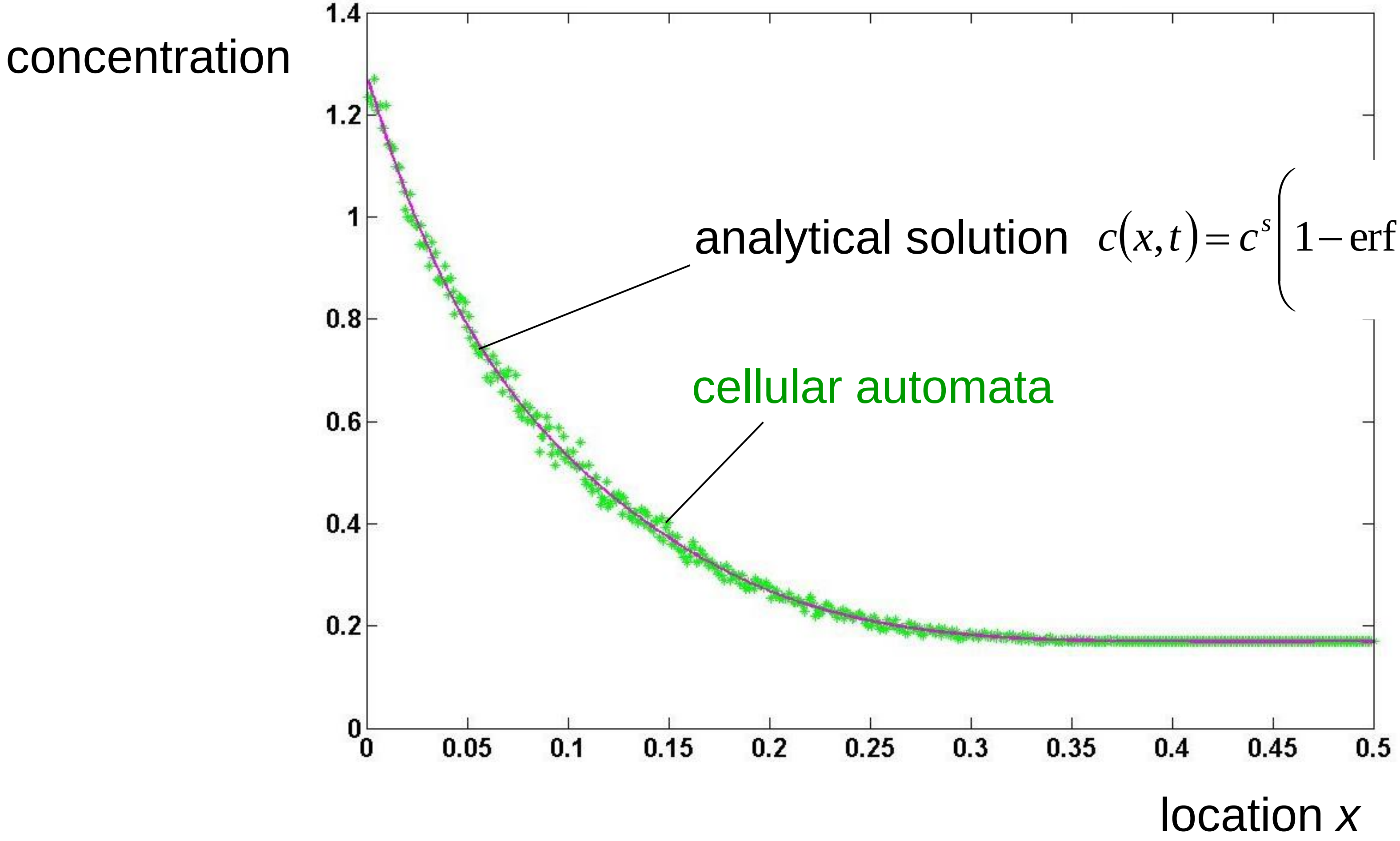
$$p_0 + 2p + p_2 = 1$$

Diffusion Coefficient

$$D_{\mathrm{N}} = \frac{\lambda^2}{\tau}\left(\frac{1}{4(p+p_2)} - \frac{1}{4}\right) = \frac{\lambda^2}{\tau}\left(\frac{p+p_0}{4(1-p-p_0)}\right) \quad \text{with} \quad \lambda = \frac{X}{n_x}, \tau = \frac{T}{n_t}$$

Chopard and Droz, Cellular Automata Modeling of Physical Problems, Cambridge Univ. Press 1998

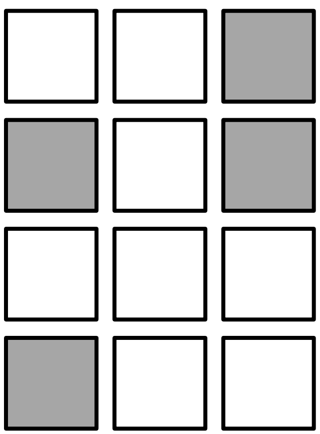
Diffusion Profile (Chopard and Droz)



$$c(x,t) = c^s \left(1 - \operatorname{erf} \frac{x}{2\sqrt{D\,t}} \right)$$

The Cellular Automata Approach for Internal Precipitation (Zhou and Wei)

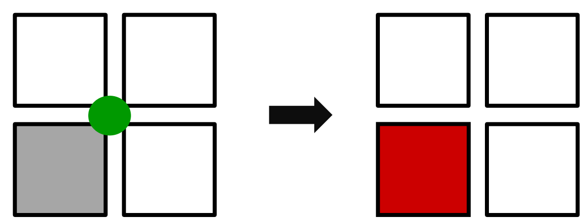
Initialization



Diffusion: N stepwise to the right

B every 20th iteration to the left

Transition: B+N=>BN: (Implementation ChemApp possible)



solvent: inert (I)

solute: active element (B)

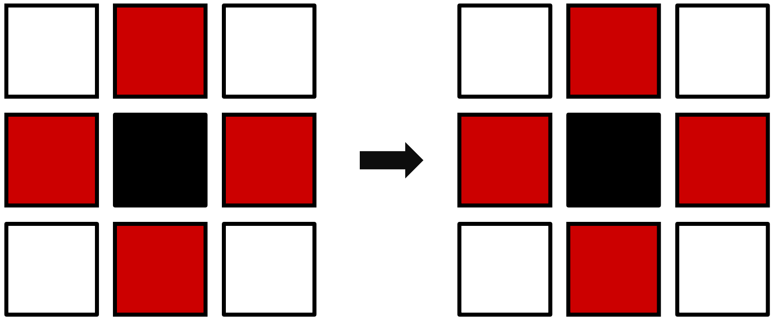
nitride (BN)

nitrogen (N)

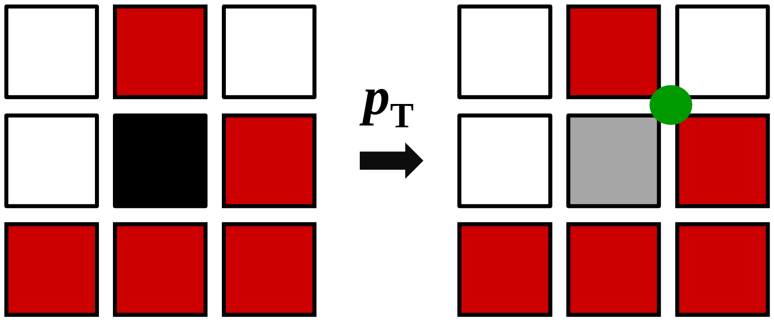
Zhou and Wei, Scripta Mater., 37 (1997) 1483

The Cellular Automata Approach for Internal Precipitation (Zhou and Wei)

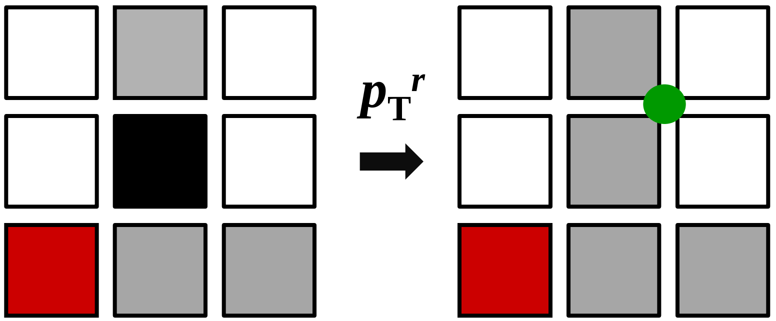
Stable state (AN)



Transition p_T:

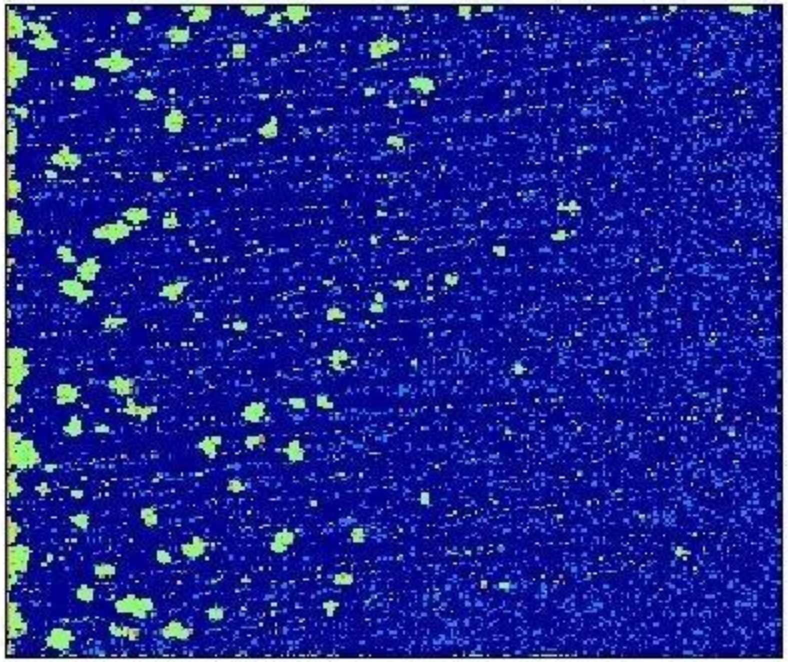


Transition p_T^r:



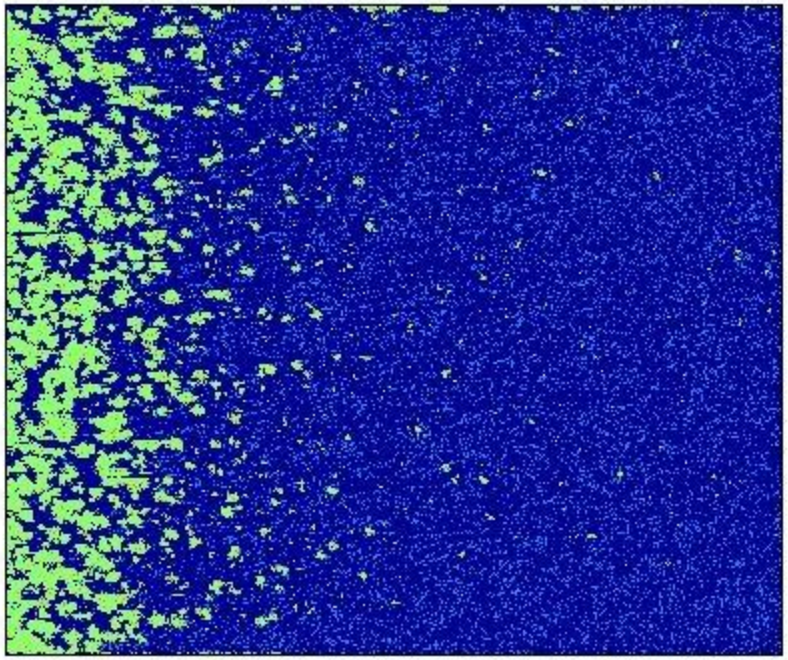
Zhou and Wei, Scripta Mater., 37 (1997) 1483

Internal Precipitation (Zhou and Wei) + N- Diffusion (Chopard and Droz)



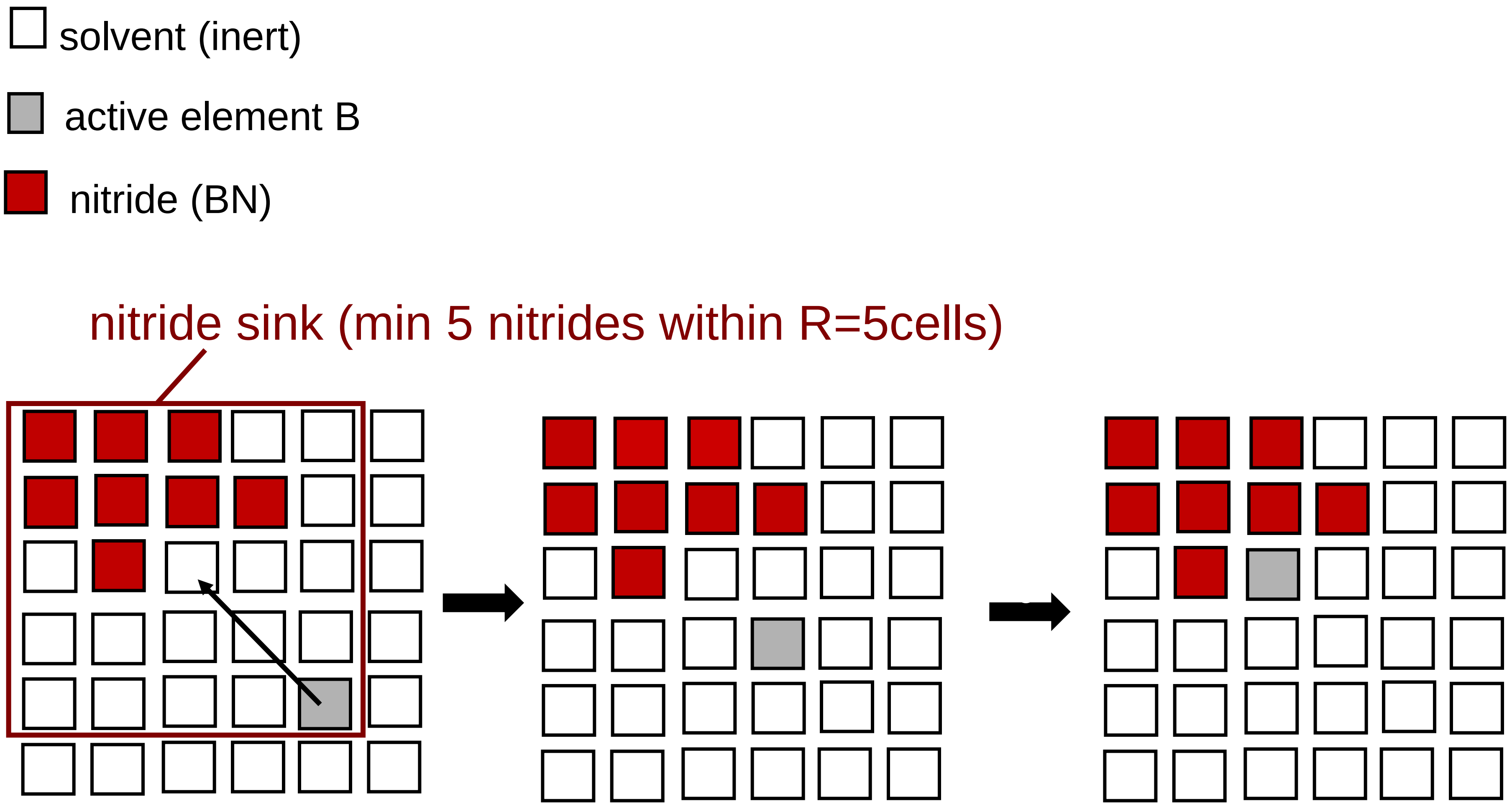
512 x 512 cells
20000 iterations

(increased B counter diffusion)

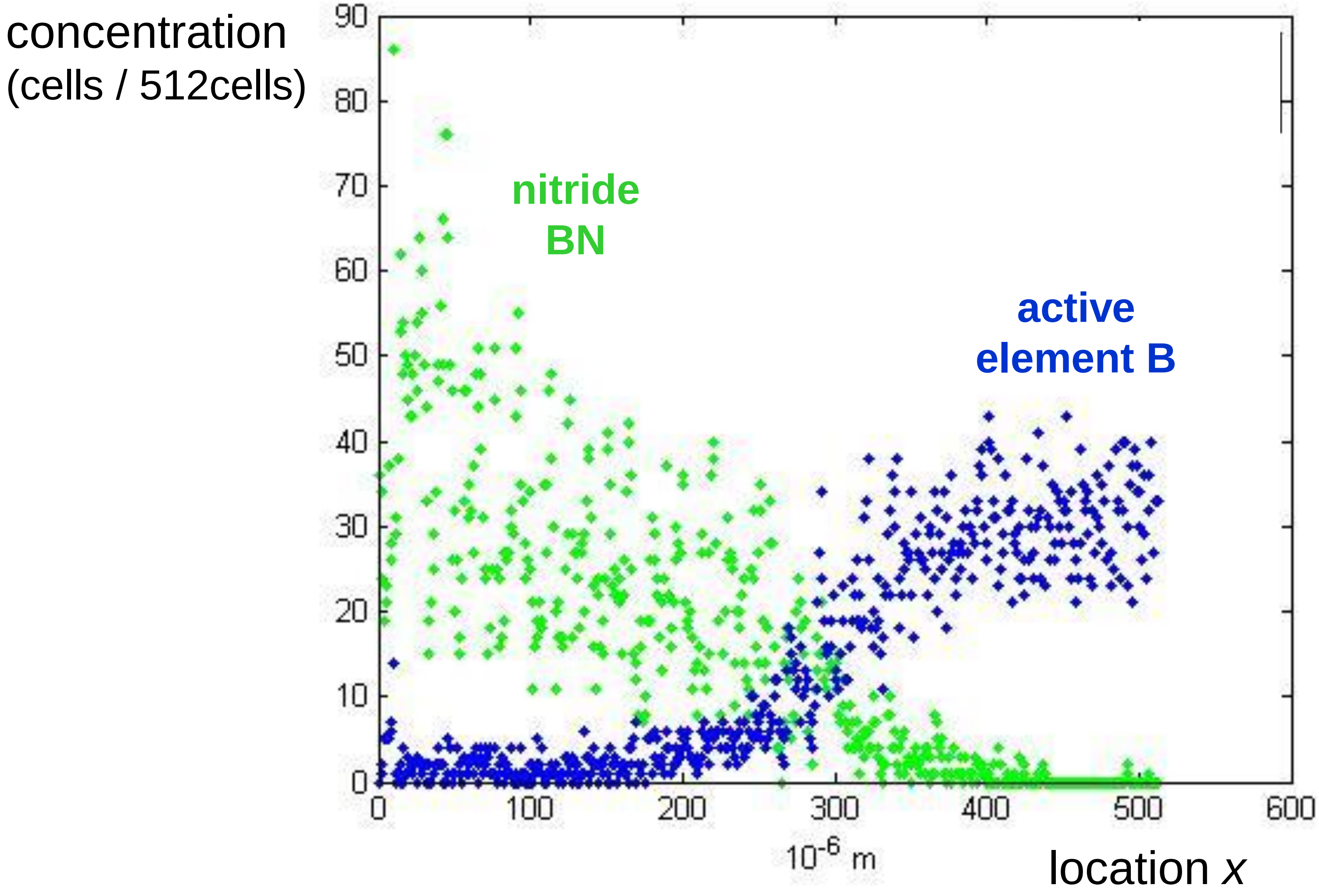


512 x 512 cells
1500 iterations

Precipitation + N Diffusion (Chopard and Droz) + B Diffusion in the Internal Precipitation Zone

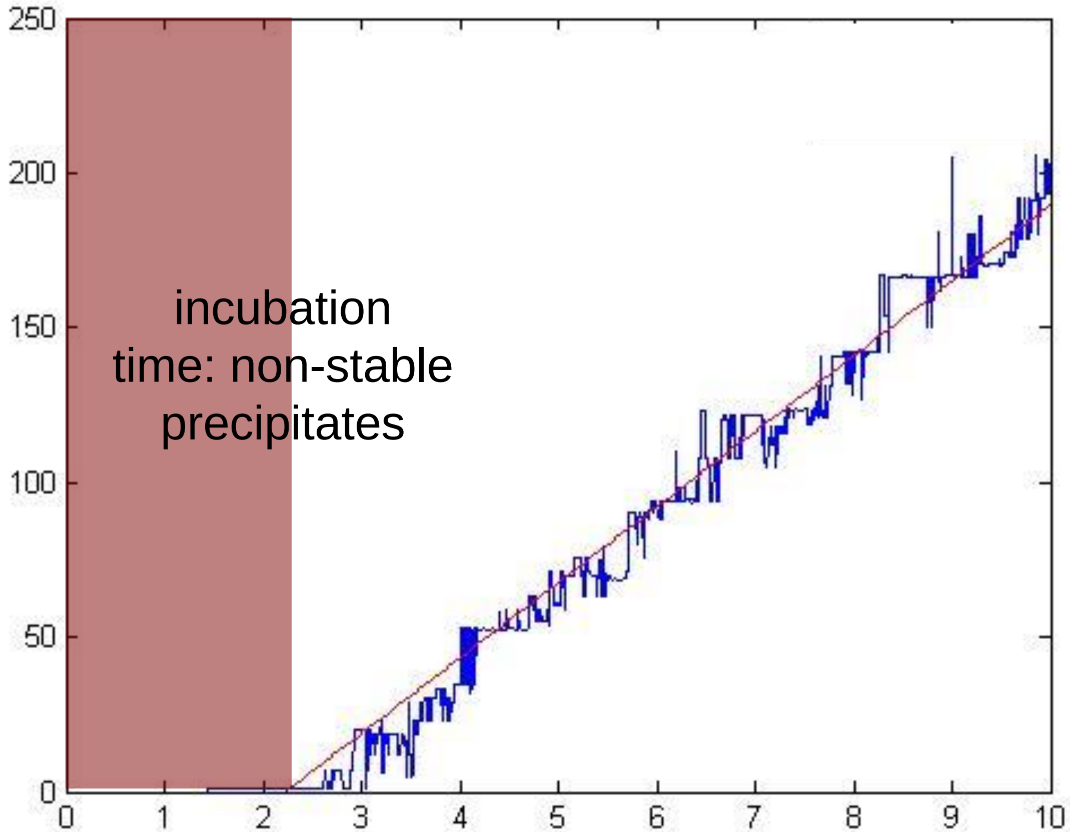


Precipitation + B Diffusion in the Internal Precipiation Zone – Concentration Profile



Precipitation + B Diffusion in the Internal Precipitation Zone – Penetration Depth

penetration depth ξ [µm]

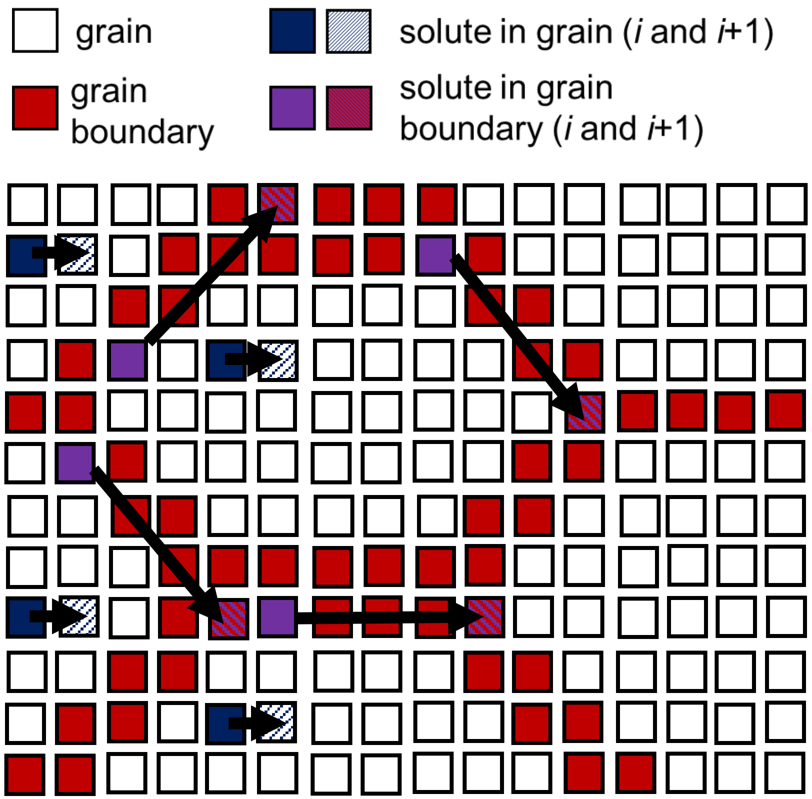


(Ni-20Cr-6Ti 1000°C, N_2)

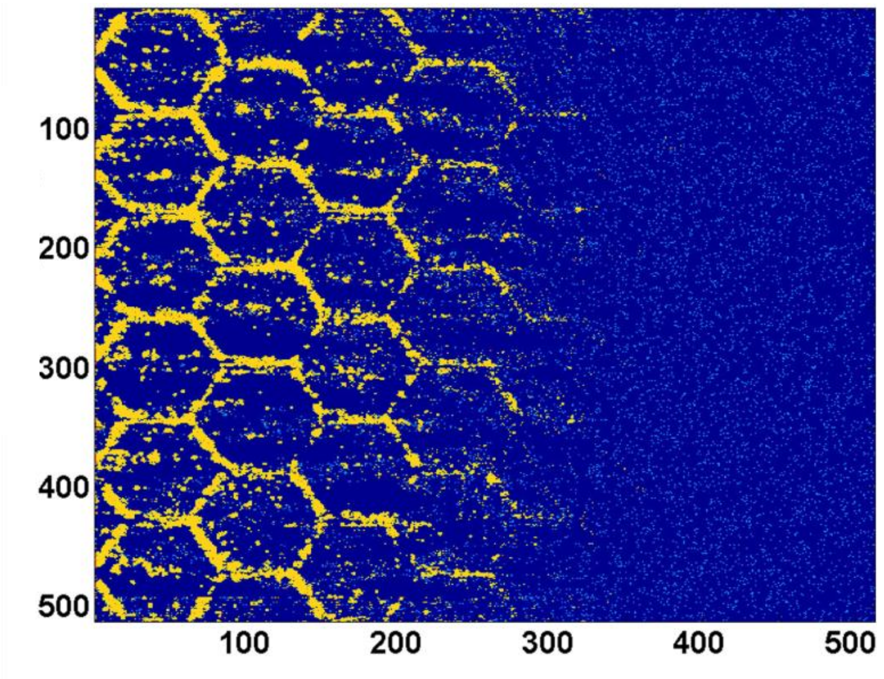
square root of exp. time [$h^{-0.5}$]

Grain boundary diffusion

$D_{GB} > D_{bulk}$



location *y*
(arbitrary units)



512 x 512 cells
3000 iterations
T_{tot}=100h, T=800°C

location *x*
(arbitrary units)

Conclusions and Future Aspects

- Classical Wagner theory is limited to special scenarios
- Finite Difference: easy combination with ChemApp
- Cellular Automata:

  -nucleation and growth

  -3D effects: various diffusion paths (e.g., GB/bulk diffusion
- Problems to be solved:

  -combination of small and large concentrations

  -implementation of ChemApp

more info: u.krupp@hs-osnabrueck.de